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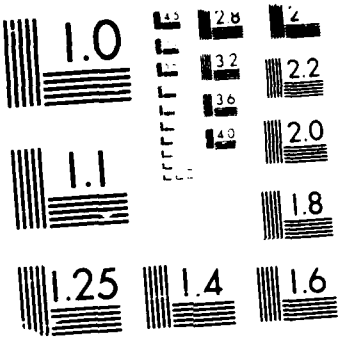

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Results of research on two novel problems in organic stereochemistry are described: 1) Topological stereochemistry; and 2) Design and synthesis of novel organic optoelectronic materials. In the topological stereochemistry project, new methods for understanding the symmetries of topologically complex molecular structures have been developed, and the total synthesis of several such structures has been achieved. New strategies for the synthesis of the first molecular knotted ring, a long sought but still illusive target, have been tested and are under development. In the optoelectronic materials project, work has focussed on design and synthesis of new ferroelectric liquid crystals (FLCs), a novel class of fluid materials possessing polar symmetry. Such materials have important potential utility in flat panel video and devices for optical computing. A predictive model for the molecular origins of the ferroelectric polarization in FLCs has been developed and demonstrated, and several new FLC classes have been invented. Also, the model is being applied to design of the first liquid phases with high second order hyperpolarizability ($\beta^{(2)}$) for ultra fast electro-optic applications.

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TOPOLOGICAL STEREOCHEMISTRY

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Part I

a. Papers submitted to Refereed Journals (and not yet published).

1. Walba, D.M.; Clark, N.A. "Molecular Design of Ferroelectric Liquid Crystals," Ferroelectrics **1988**, in press. Other support: NSF, IBM.

2. Walba, D.M.; Simon, J.; Harary, F. "Topicity of Vertices and Edges in the Möbius Ladders: A Topological Result with Chemical Implications," Tetrahedron Lett. **1988**, in press.

b. Papers Published in Refereed Journals.

1. Walba, D.M. "Topological Stereochemistry," Tetrahedron **1985**, 41, 3161-3212.

2. Walba, D.M.; Armstrong, J.D., III; Perry, A.E.; Richards, R.M.; Homan, T.C.; Haltiwanger, R.C. "The THYME Polyethers: An Approach to the Synthesis of a Molecular Knotted Ring," Tetrahedron **1986**, 42, 1883-1894.

3. Walba, D.M.; Slater, S.C.; Thurmes, W.N.; Clark, N.A.; Handschy, M.A.; Supon, F. "Design and Synthesis of a New Ferroelectric Liquid Crystal Family. Liquid Crystals Containing a Non-Racemic 2-Alkoxy-1-Propoxy Unit," J. Am. Chem. Soc. **1986**, 108, 5210-5221. Other support: NSF.

3. Walba, D.M.; Vohra, R.T.; Clark, N.A.; Handschy, M.A.; Xue, J.; Parmar, D.S.; Lagerwall, S.T.; Skarp, K. "Design and Synthesis of New Ferroelectric Liquid Crystals. 2. Liquid Crystals Containing a Non-Racemic 2,3-Epoxy Alcohol Unit," J. Am. Chem. Soc. **1986**, 108, 7424-7425. Other support: NSF.

4. Walba, D.M.; Richards, R.M.; Hermsmeier, M.; Haltiwanger, R.C. "Conformational Properties of the THYME Polyethers: The Bis-THYME Cylinder—a 3-Dimensional Analogue of 18-Crown-6," J. Am. Chem. Soc. **1987**, 109, 7081-7087.

5. Walba, D.M. "Topological Stereochemistry: Knot Theory of Molecular Graphs," Stud. Phys. Theor. Chem. **1987**, 51, 23-42.

c. Books (and sections thereof) Submitted for Publication.

none

d. Books (and sections thereof) Published.

none

e. Technical Reports Published and Papers Published in Non-Refereed Journals.

1. Walba, D.M.; Perry, A.E.; Homan, T.C.; Armstrong, J.D. III, "Synthesis and Stereochemistry of Molecular Knots, Links and Möbius Strips," Abstracts of the Creative Work in Organic Chemistry Symposium at the 189th American Chemical Society National Meeting, Miami Beach, Florida, April 30, 1985.

2. Andersson, G.; Dahl, I.; Lagerwall, S.T.; Skarp, K.; Clark, N.A.; Handschy, M.A.; Walba, D.M. "Physical Properties of the Ferroelectric Phase in Some Fast-Switching Chiral Epoxy Compounds and lactic Ethers," Abstracts of the 11th International Liquid Crystal Conference, Berkeley, California, June 30-July 4, 1986, θ-033-FE. Other support: NSF.

3. Razavi, H.A.; Walba, D.M.; Parmar, D.S.; Clark, N.A.; Wand, M.D. "Synthesis of Ferroelectric Liquid Crystals Containing the 2-Alkoxy-1-Propoxy Unit," Abstracts of the 11th International Liquid Crystal Conference, Berkeley, California, June 30-July 4, 1986, θ-038-FE. Other support: NSF.

4. Vohra, R.T.; Walba, D.M.; Parmar, D.S.; Clark, N.A. "Synthesis and Some Properties of a New Class of Ferroelectric and Chiral Nematic Liquid Crystals Containing the 2,3-Epoxy Alcohol Unit," Abstracts of the 11th International Liquid Crystal Conference, Berkeley, California, June 30-July 4, 1986, θ-039-FE. Other support: NSF.

5. Eidman, K.; Walba, D.M.; Parmar, D.S.; Clark, N.A. "Synthesis of Ferroelectric Liquid Crystals Containing a Non-Racemic Cyanohydrin Ether Tail Unit," Abstracts of the 11th International Liquid Crystal Conference, Berkeley, California, June 30-July 4, 1986, θ-040-FE. Other support: NSF.

6. Walba, D.M.; Clark, N.A. "A Model for the Molecular Origins of the Ferroelectric Polarization in Ferroelectric Liquid Crystals," Abstracts of the 11th International Liquid Crystal Conference, Berkeley, California, June 30-July 4, 1986, θ-041-FE. Other support: NSF.

7. Walba, D.M., Simon, J. "Topological Stereochemistry: Knot Theory of Molecular Graphs," Abstracts of the American Association for the Advancement of Science 153rd National Meeting: Symposium on Knotting Phenomena in the Natural Sciences, Chicago, Illinois February 16, 1987.

8. Walba, D.M.; Vohra, R.T.; Razavi, H.A.; Eidman, K.; Clark, N.A.; Handschy, M.A.; Parmar, D.S. "Using the Host-Guest Paradigm in Liquid Crystal Chemistry: A Model for the Molecular Origins of the Polarization in Ferroelectric Liquid Crystals," Abstracts of the 193rd ACS National Meeting, Denver, Colorado, April 9, 1987. Other support: NSF, IBM.

9. Walba, D.M.; Clark, N.A. "Model for the Molecular Origins of the Polarization in Ferroelectric Liquid Crystals," Proc. SPIE **1988**, 825, in press. Other support: NSF, IBM.

f. Patents Filed.

1. Walba, D.M.; Razavi, H.A. "Ferroelectric Liquid Crystal Compounds and Compositions," U.S. Patent Application No. 099,079, filed September 21, 1987. Other support: NSF, IBM.

g. Patents Granted.

none

h. Invited Presentations at Topical or Scientific/Technical Society Conferences.

1. The Organic Topical Group, North Jersey Section of the American Chemical Society, Seton Hall University, "Topological Stereochemistry: The Total Synthesis of Molecular Links, Knots, and Möbius Strips," February 25, 1985.

2. Creative Work in Organic Chemistry Symposium at the 189th American Chemical Society National Meeting, Miami Beach, Florida, "Synthesis and Stereochemistry of Molecular Knots, Links, and Möbius Strips," April 30, 1985.

3. Colorado Section of the American Chemical Society, Colorado College, Colorado Springs "Topological Stereochemistry: Synthesis of Molecular Knots, Links, and Möbius Strips," September 12, 1985.

5. Symposium on Knotting Phenomena in the Natural Sciences, University of Illinois at Chicago, "Stereochemical Topology," February 14, 1987.

6. American Association for the Advancement of Science 153rd National Meeting: Symposium on Knotting Phenomena in the Natural Sciences, "Topological Stereochemistry: Knot Theory of Molecular Graphs," February 16, 1987.

7. Conference on Graph Theory and Topology in Chemistry, University of Georgia, Athens, Georgia,"Topological Stereochemistry: Knot Theory of Molecular Graphs," March 16, 1987.

8. Euchem Stereochemistry Conference, Bürgenstock, Switzerland,"Design of High Performance Ferroelectric Liquid Crystals," May 8, 1987. Other support: NSF, IBM.

9. Physical Organic Gordon Conference, Holderness School, Plymouth, New Hampshire "Design of High Performance Ferroelectric Liquid Crystals: A Model for the Molecular Origins of the Polarization in FLCs," June 16, 1987. Other support: NSF, IBM.

10. Liquid Crystals Gordon Conference, Brewster Academy, Wolfeboro, New Hampshire "Design of High Performance Ferroelectric Liquid Crystals," June 22, 1987.

11. 1st International Symposium on Ferroelectric Liquid Crystals, Bordeaux-Arcachon, France "Molecular Design of Ferroelectric Liquid Crystals," September 21, 1987. Other support: NSF, IBM.

i. Contributed Presentations at Topical or Scientific/Technical Society Conferences.

1. 11th International Liquid Crystal Conference, Berkeley, California, "A Model for the Molecular Origins of the Ferroelectric Polarization in Ferroelectric Liquid Crystals," Poster presentation July 3, 1986. Other support: NSF.

2. Walba, D.M. "Using the Host-Guest Paradigm in Liquid Crystal Chemistry: A Model for the Molecular Origins of the Polarization in Ferroelectric Liquid Crystals," 193rd ACS National Meeting, Denver, Colorado, April 9, 1987. Other support: NSF, IBM.

3. Walba, D.M.; Clark, N.A. "Model for the Molecular Origin of Polarization in Ferroelectric Liquid Crystals," 31st Annual International Technical Symposium on Optical & Optoelectronic Applied Science & Engineering, Conference on Spatial Light Modulators and Applications, San Diego, California, August 17, 1987. Other support: NSF, IBM.

j. Honors/Awards/Prizes.

1. Camille and Henry Dreyfus Teacher-Scholar, 1984-1986.

2. University of Colorado Faculty Fellowship, 1988-1989.

k. Graduate Students Receiving Full or Partial Support on ONR Contract.

Joseph D. Armstrong, III; Ann E. Perry; Timothy C. Homan; Mark Hermsmeier; Homaune A. Razavi; Kirk Eidman; Qun Yi Zeng.

j. Postdoctoral Fellows and Technicians Receiving Full or Partial Support on ONR Contract.

Postdoctorals: David Wasserman; Bengt Otterholm; Wen-Liang Tsai; Technician: Rohini T. Vohra.

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Summary of Results

Two major research problems are under investigation: 1) Topological Stereochemistry; and 2) Design and Synthesis of Novel Organic Optoelectronic Materials. The former project is directed towards the synthesis of organic molecules possessing novel low-dimensional topology. Targets include molecular Möbius strips, linked rings, and knotted rings, using the tetrahydroxymethylethylene (THYME) fused crown ether strategy illustrated by our synthesis of the first molecular Möbius strip. In addition to the synthetic work, theoretical investigations on the consequences of non-trivial topology of molecular graphs on stereoisomerism are under way. In the second project, research focuses on the design and synthesis of new ferroelectric liquid crystals for use in display devices and spatial light modulators for optoelectronic computing systems. Knowledge gained in this field may also be applied to design of a novel class of organic materials for second order nonlinear optics applications with ultra-fast (<1 psec) response. Results in each of these projects are summarized below.

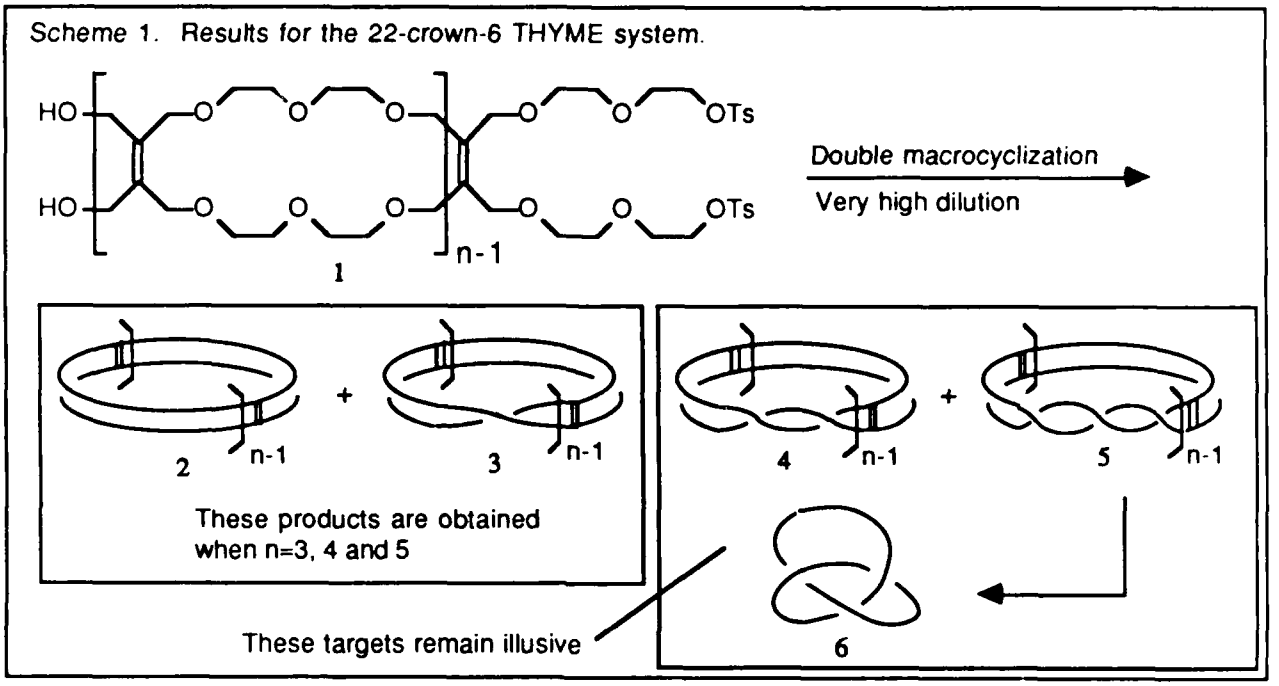
Topological Stereochemistry. Most molecules possess topologically simple structures in the sense that their molecular graphs are planar, polygonal nets with no novel low-dimensional topological properties. When considering the symmetry properties of such molecules—used to predict simple physical observables such as NMR spectra—Euclidean geometry plays a dominant role. Modern techniques in organic and inorganic synthesis, however, make molecules with topologically complex structures realizable. To understand the symmetry properties of large, very flexible molecules with novel topology, such as those synthesized in our own group as part of this project, new methods are required.

In collaboration with Professor Jonathan Simon, this interesting problem has been solved with the invention of the topological symmetry concept applied to molecular structures, and techniques for calculation of the topological symmetry group of a structure. Since, under conditions where bonds are not made or broken, the topological symmetry of a molecular graph is an absolute upper bound on the symmetry of any molecular realization of that graph, properties of molecules which previously could only be guessed can now be proven in a geometrically rigorous way. This work has been described in a preliminary manner is several publications, and a manuscript outlining in detail the method and its application to chemical problems is in preparation.

During the past several years the major emphasis of our work in topological stereochemistry has been directed towards synthesis of new molecular structures with novel topology. The classic targets in this field, which has quite a long and interesting history, are molecular linked rings, knotted rings, and Möbius strips. The first molecular linked rings were synthesized by Wasserman in 1959, and Sauvage has recently developed methods for extremely elegant and efficient synthesis of linked rings of atoms.

Our work in this field began with the synthesis of the first molecular Möbius strip in 1982. Interestingly, while several groups have directed considerable efforts towards preparation of a molecular knotted ring, to date this most classic of all topological targets remains illusive.

The THYME polyether approach to the synthesis of Möbius strips, links and knots, developed in our labs, is illustrated in Scheme 1. The overall strategy and details of work in the two, three and four rung cases (n=2,3, and 4) has been described in several publications. For n=4, cyclization of diol-ditosylate **1** gave only two identifiable products, with zero and one half twist (**2** and **3**, respectively). Unpublished recent results indicate that the five rung system behaves analogously—that is, no products with two and three half twists (**4** and **5**) have been isolated. Even so, note that the five rung Möbius ladder **3** (n=5) has a single edge of an even 100 atoms!



Experimentally, work in the five-rung THYME system pushes the frontiers in methods for analysis of reaction products. With molecular weights well over 1,000, the molecules under investigation are in essence exact molecular weight polymers, and conventional methods of functional group analysis often fail. Progress in the project has been possible mainly due to the excellent technique of fast atom bombardment (FAB) mass spectrometry. In the THYME system, we noticed that ions corresponding to $(P+Na)^+$ and $(P+K)^+$ are often observed. Upon doping the FAB matrix with Rb^+ and Cs^+, cationic complexes of these ions are also observed. This led to an interesting study of the ion selectivity profiles of the various polyethers. Interestingly, in the three-rung system (but not with four or five rungs), the Möbius ladder (**3**, n=3) possesses a very different selectivity profile from the cylindrical product (**2**, n=3).

In order to better understand the properties of the THYME polyethers, a computerized molecular modelling study has been started. Interesting results in the two-rung system using MM2 force fields have been published. Modelling now is focussing on application of the exciting CHARM program for dynamics studies. Calculations can be compared with NMR experiments giving the effective activation barriers for the "inside-out" motion of the cylinders **2** (n=4, and n=5), affording an excellent check on the modelling technique. If the calculations are shown to be valid for the cylinders, then the novel "twist motion" of the Möbius ladders, known to occur with a low activation energy, can be modelled.

In order to achieve our ultimate goal, synthesis of the first molecular knotted ring, two alternatives to the THYME strategy outlined in Scheme 1 are under investigation. Based upon the

assumption that the rigidity of the double bond units ladders of type **1** is inhibiting the desired twist (i.e. the intermediates leading to the two and three half-twist products are too strained—an hypothesis which can be "tested" using the molecular modelling techniques described above), studies in the homologous 28-crown-8 THYME system are in progress. In this more flexible system the two rung diol-ditosylate led to formation of the first two rung "Möbius ladder". Experiments directed towards synthesis of a four rung homologue, which is hoped to give the three half twist product, are under way.

It is possible, however, that no matter how long the ladder, or how long the edges separating the rungs of the ladder, the THYME system will never give the desired three half-twist product. We have recently developed a strategy—called the hook and ladder—which leads to a trefoil knot (structure **6**) with only one half-twist! This strategy is briefly described in our 1987 publication in Stud. Phys. Theor. Chem., and considerable progress has been made towards its realization using Sauvage's molecular "hooks" combined with the THYME ladders.

Finally, it is interesting to note that two half-twists in the hook and ladder affords a molecular figure of eight knot—until now an "impossible" target. Indeed, the actual figure of eight obtained in the hook and ladder is a topological rubber glove, a very novel object first conjectured in the context of this project. A synthesis of the first topological rubber glove would be a fitting conclusion to the topological stereochemistry project.

Optoelectronic Materials. Since 1986 we have broadened the scope of the ONR funded project in our group to include studies on design and synthesis of new organic optoelectronic materials—an exciting new direction in organic stereochemical research. Specifically, work has focussed on design and preparation of high performance ferroelectric liquid crystal (FLC) materials. These novel fluids—the only liquid phases known which possess polar symmetry—are central to an emerging technology based on the surface stabilized ferroelectric liquid crystal (SSFLC) light valve. The SSFLC device, invented by physics professor Noel Clark (a co-PI on the project with Professor Walba), has operating parameters *unachievable with any other technology* (high contrast, μsec switching speeds, bistability, very low switching energy, and a sharp threshold), as described in several recent publications.

In order to realize the potential of the SSFLC technology for large area flat panel video displays, spatial light modulators for optoelectronic computing applications, and other devices, improvements in every aspect of the technology are required. Our work, of course, focuses on the FLC materials themselves. We have developed the first predictive model for the molecular origins of the polarization in FLCs (an important contributor to the switching speed achievable), based upon the concept that the polarization is a novel manifestation of a kind of molecular recognition occurring in the phase. This has also been described in publications, and the basic tenets of the model have been proven in exciting recent experiments. This work has also led to the synthesis of several excellent FLC component classes—five patents have issued, one is pending, and several are in preparation.

Our model basically affords an understanding and some control over orientation of organic functional groups relative to the laboratory frame in a liquid phase. While application of this paradigm to design of FLC materials with improved properties is an important goal, ultimately we plan to use these insights into molecular orientation to design the first liquids with high second order nonlinear hyperpolarizability $\chi^{(2)}$. Success in this project would make possible the easy fabrication of devices requiring thin films ($\cong 2\mu m$ thick) of $\chi^{(2)}$ material over large areas for use in ultra-fast (sub-psec) integrated electro-optic devices such as wave-guide structures.

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